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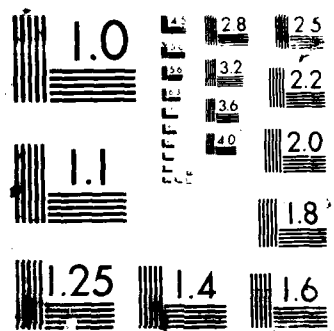
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Polymer - Ceramic Composites

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Principal Investigator: Dilip K. Das-Gupta,
School of Electronic Engineering
Sciences,
Dean Street,
Bangor,
Gwynedd LL57 1UT
U.K.

Telephone: (0248) 351151 Ext. 2696

Fax: (0248) 361429

Telex: 61100 UCNWSL G

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ABSTRACT: Composites of Lead Zirconate Titanate (PZT) and polyvinylidene fluoride (PVDF) were prepared and its electrical and dielectric behaviours were analysed. PZT phase has been suggested to have a significant contribution on the electrical conduction and low frequency dielectric loss at high temperatures. The pyroelectric behaviour obtained from composites of different materials may suggest that the elastic stiffness and thermal expansion of the polymer matrix were among the factors contributing to the measured pyroelectric activity. A higher pyroelectric figure of merit as compared to PZT has been achieved in one of the PZT/PVDF composites.

The previous reports provide experimental data and analysis of the dielectric behaviour of PVDF/PZT polymer-ceramic composite films (prepared in our laboratories in which 75% volume fraction of PZT powder had been introduced in the matrix of the host polymer PVDF) in the frequency range of 10^{-4} Hz to 65 kHz.

Present report provides the results of a study of the electroactive (absorption current, dielectric dispersion and pyroelectric coefficient) properties of (i) PZT5/PVDF (50/50), (ii) PZT8/PVDF (50/50). PVDF is a copolymer of VDF/TrFE and PVDF is a homopolymer of polyvinylidene fluoride. The characteristic properties of our composite films are then compared with those of Piezel, a commercially available composite, manufactured by the Daikin Industry Limited of Japan.

Composite samples are prepared from PZT ceramic powder (PZT5 and PZT8, supplied by Unilator, U.K.) mixed up with PVDF pellets (PVDF(A) is solef 11010 and PVDF(B) is solef 1008, obtained from Laporte Trad., U.K.) at 443K using a hot roller machine and then pressing into film of 250 μm in a temperature-controlled hydraulic press. After depositing an aluminium electrode of 2cm x 2 cm on both sides of the film, the samples were thermally treated in an evacuated measurement chamber ($<10^{-5}$ torr) at 373K for ~24 hours before any measurements were performed. The dielectric permittivity and the dielectric loss were measured using a General Radio Bridge or a Solartron FRA. Pyroelectric activity was measured by a direct method (Byer and Roundy 1972), in which a linear heating rate of 1°C/min is employed. The pyroelectric responses were also studied by a dynamic method (Simhony and Shaulov 1971, Das-Gupta and Doughty 1980) by exposing the samples to a well focused light from a tungsten filament. Some results obtained on PIEZEL (composite of PZT and PVDF copolymer, supplied by Daikin Industries Limited of Japan) are also presented.

3. RESULTS AND DISCUSSIONS

The time dependence of charging currents in PZT/polymer composites are shown in Figure 1. It may be observed that in all cases the currents decreasing monotonously with the time at different rates of decay. However, for the two upper curves which were obtained using different types of PZT and different PVDF grades of equal volume percentage between ceramic and polymer phases, the difference is not so significant. The current in PIEZEL sample was observed to reach steady state level in the region of $\sim 10^5$ sec whereas in the prepared composites the time taken is shorter. Indeed, the steady state level could be reached at earlier times as the temperature and field are increased. The analysis of the steady state current in the composites showed that its behaviour is governed by an ionic hopping mechanism with a substantial contribution from PZT phase at high temperatures (Das-Gupta and Abdullah 1986, Das-Gupta and Abdullah 1987).

Figure 2 shows the behaviour of the dielectric permittivity and loss in the composites. In the high frequency region, the values of ϵ' are about the same for all composites but at the lower frequencies, their values tend to differ significantly. The calculated permittivities of the prepared composites using the equation given by Yamada et al (1982) are in good agreement with the observed values (Das-Gupta and Abdullah 1987). The dielectric loss behaviour shows a broad peak in the region 10^3 - 10^4 Hz which may be due to the relaxation of the polymer phase which occurs at similar frequencies and temperature region. The high dielectric loss at lower frequencies seemed to be significantly due to PZT phase as had been revealed in the previous results (Abdullah and Das-Gupta 1987, Das-Gupta and Abdullah 1987).

The large difference of losses at lower frequencies between those composites may be due to the different types of PZT being employed which may arise from their differences in microstructures (domain walls, crystallite size and grain boundaries). Furthermore, the added impurities (which are usually present and of different kinds for different PZT types) into the PZT phase may also cause such a big difference of ϵ'' values (Lines and Glass 1979).

The pyroelectric coefficients as a function of temperatures obtained by the direct method in the composites are shown in Figure 3 from which it may be observed that the sample with highest losses showed a very low $p(T)$ at lower temperatures region, whereas the other two samples appear to have similar $p(T)$ values. Factors such as elastic stiffness and thermal expansion of the polymer and the interconnection and internal stresses may contribute significantly to the observed differences in $p(T)$ values of the present results, in the same manner as the result of Galgoci et al (1986) showed. For composite PZT5/PVDF(A), although the value of $p(T)$ at 343K is only 9×10^{-5} Coul/m²/K which is lower than that of PZT ($p(T) = 50 \times 10^{-5}$ Coul/m²/K) at the same temperature, its pyroelectric figure of merit $p(T)/\epsilon'$ is 2.5 times higher than that of PZT (taking $\epsilon'(\text{Composite})=95$, $\epsilon'(\text{PZT})=1300$). Figure 4 shows the pyroelectric peak current $I_{p\max}$ obtained by the dynamic method as a function of poling fields at 373 K and 333 K in PZT5/PVDF(A). It may be observed that the data shows an approximately linear relationship at the temperatures and within the range of fields of the measurements. Obviously efficient poling is achieved at high temperatures and fields as long as it does not reach the breakdown

field of the samples. Further measurements on PZT5/PVDF(A) established a linear relationship between I_{pmax} and $p(T)$ at 333K (see Figure 5) as:

$$I_{pmax} = Kp(T) \quad (1)$$

where $K = 2.1 \times 10^{-5} \text{ m}^2 \cdot \text{s}^{-1} \cdot ^\circ\text{K}$, which could be considered as a constant for the same sample material having the same electrode geometry with the incident light power and the electrical and thermal time constant of the system remain unchanged.

In conclusion, the steady state conduction of PZT/PVDF composites and its dielectric loss in the low frequencies region at high temperatures are significantly controlled by PZT phase. A higher pyroelectric figure of merit has been achieved in one of the composites of PZT/PVDF as compared to single phase PZT.

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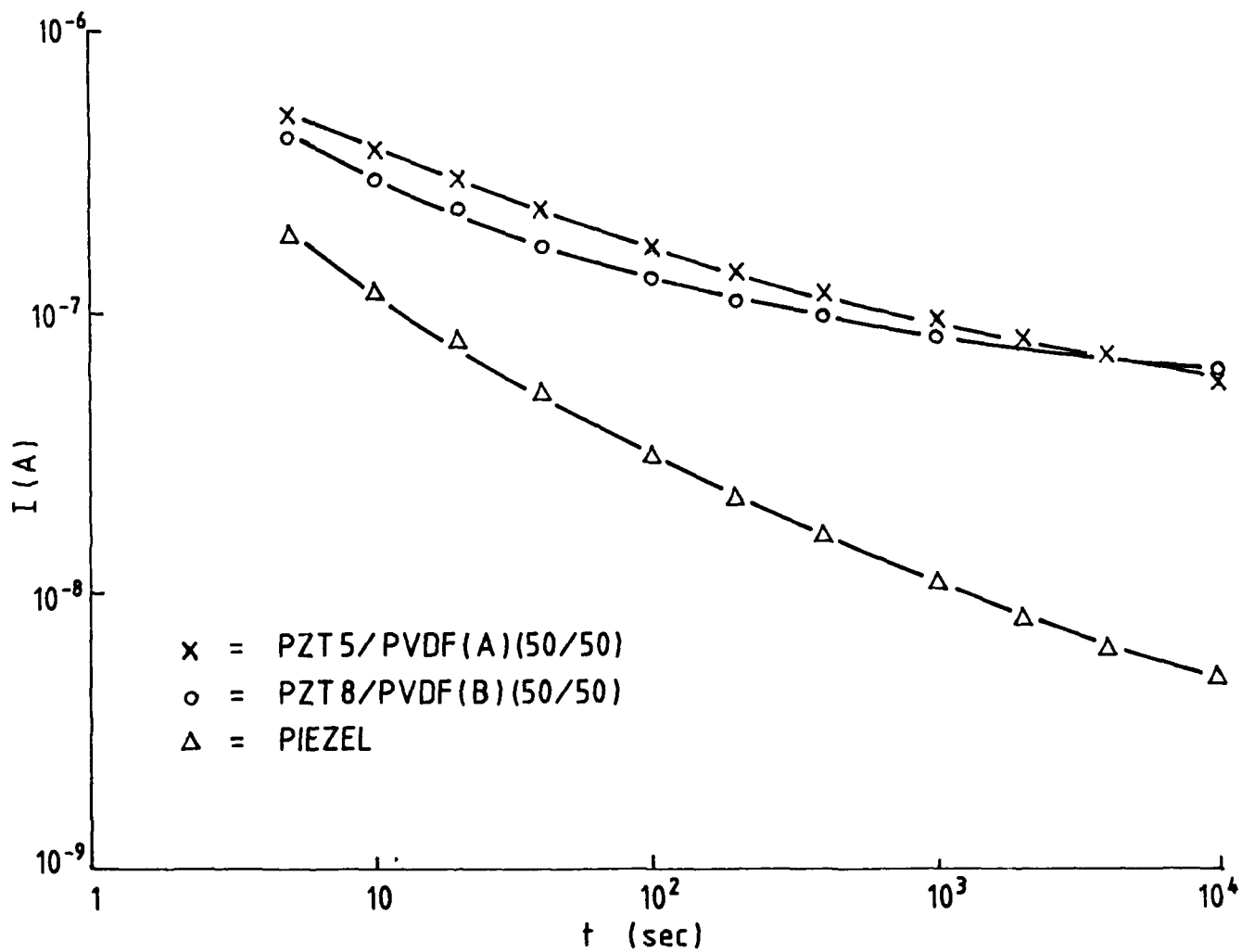


Fig. 1: Charging currents in PZT/PVDF and PIEZEL at 363 K and field $1.75 \times 10^6 \text{ Vm}^{-1}$.

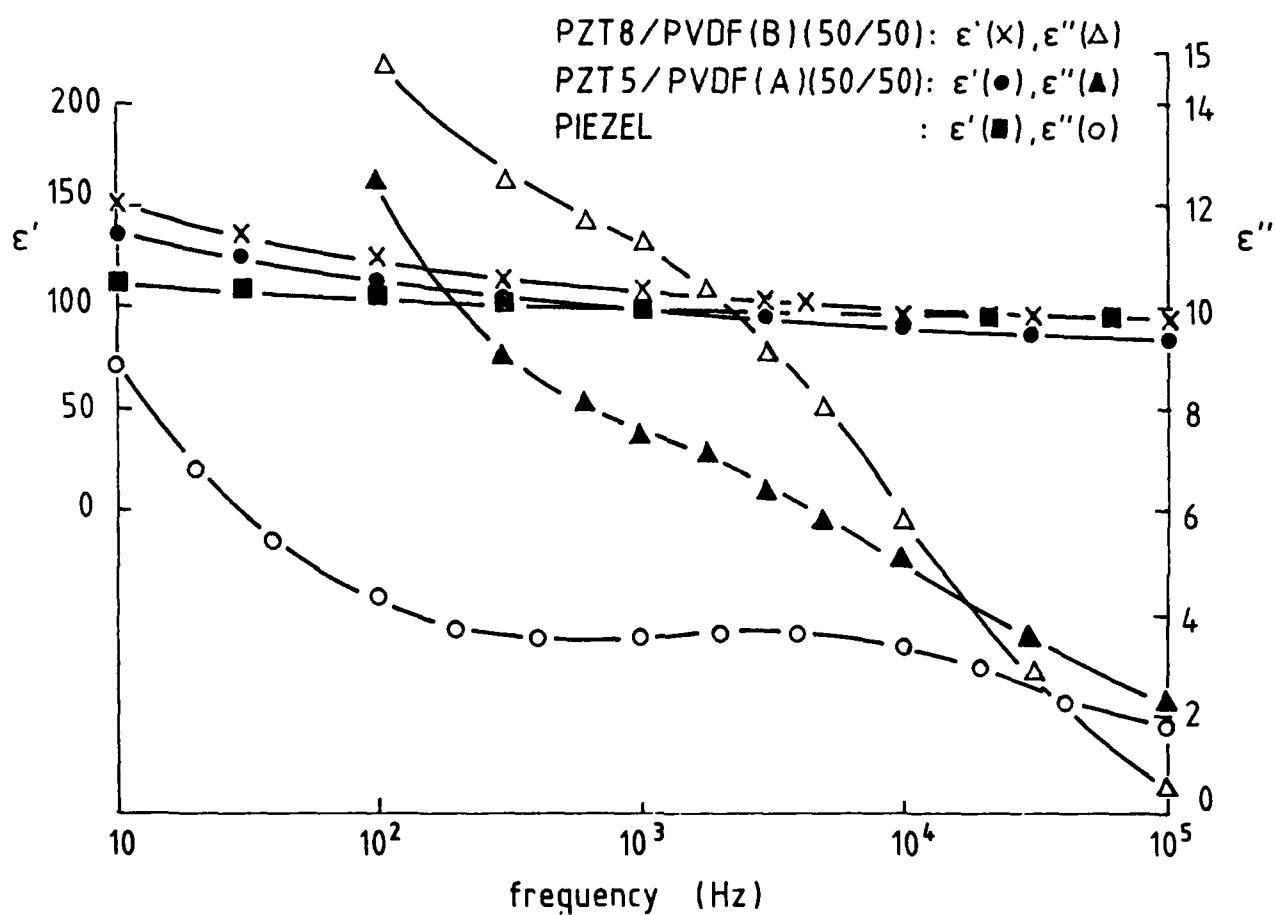


Fig. 2: The behaviour of ϵ' and ϵ'' against frequency in PZT /PVDF and PIEZEL at 363 K.

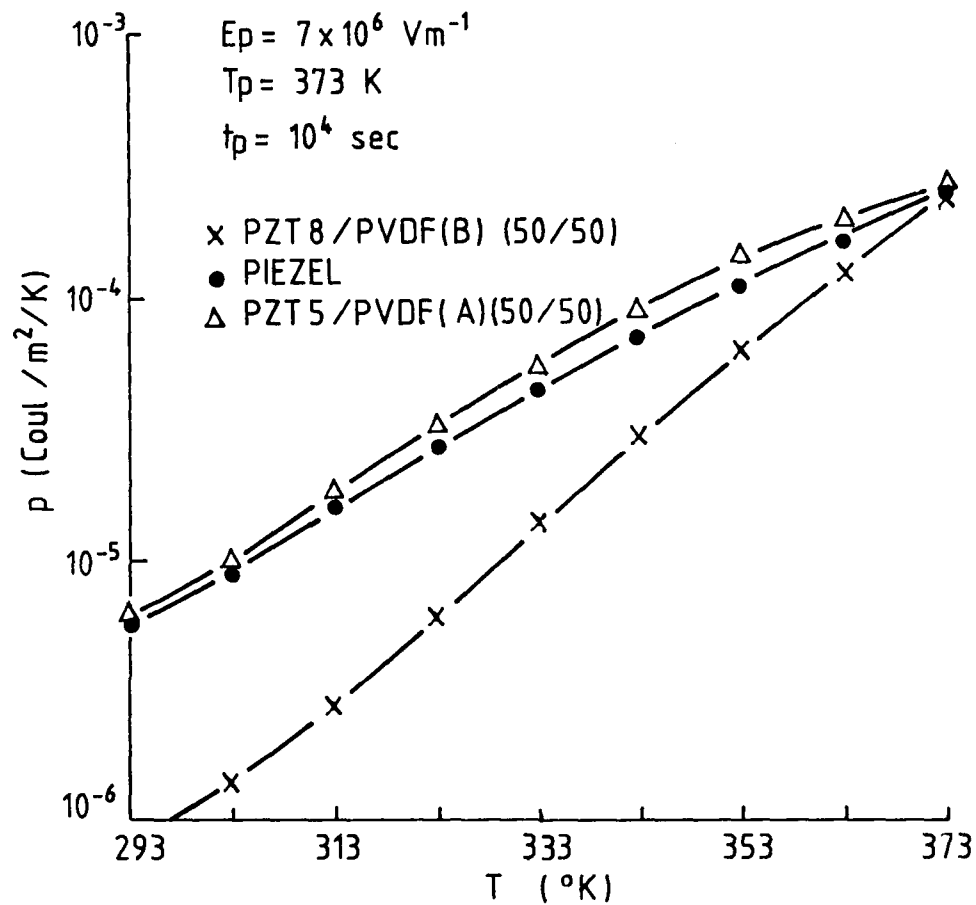


Fig. 3: Pyroelectric coefficient against temperature in PZT/PVDF and PIEZEL.

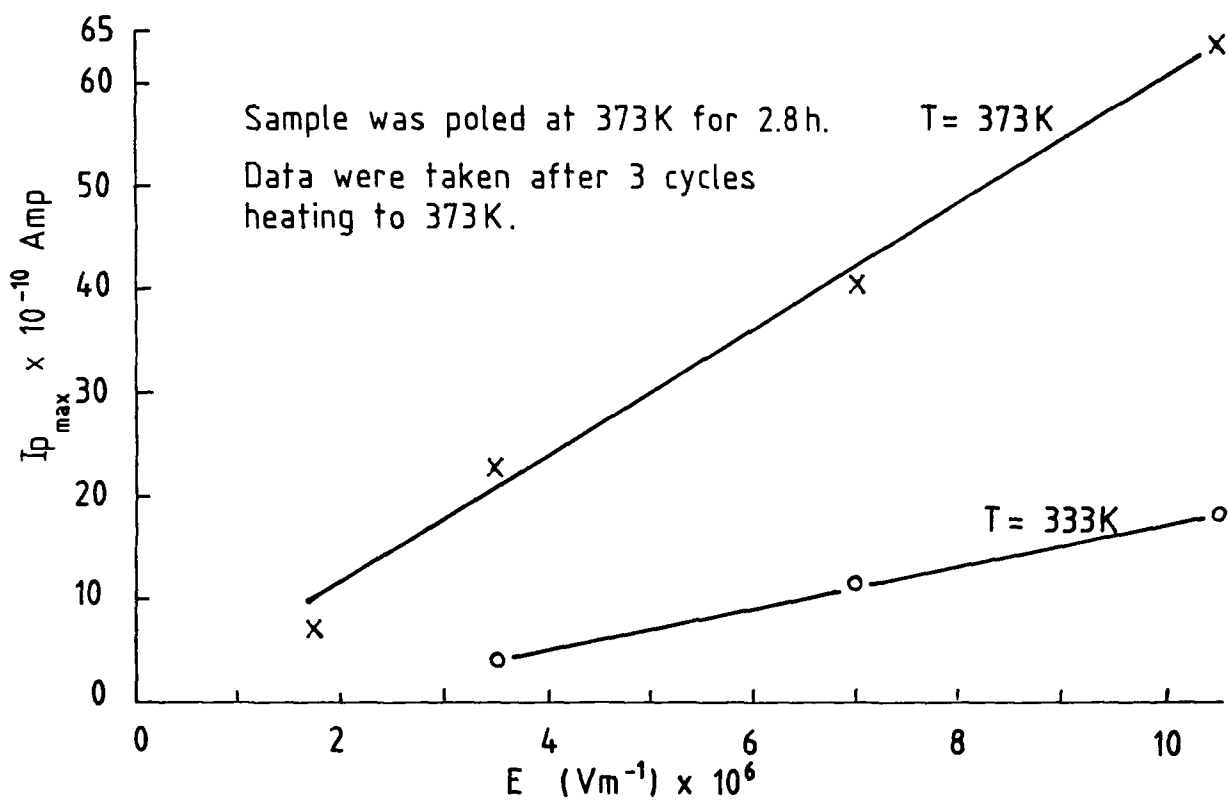


Fig. 4: Peak current against poling field in PZT5/PVDF (A)(50/50).

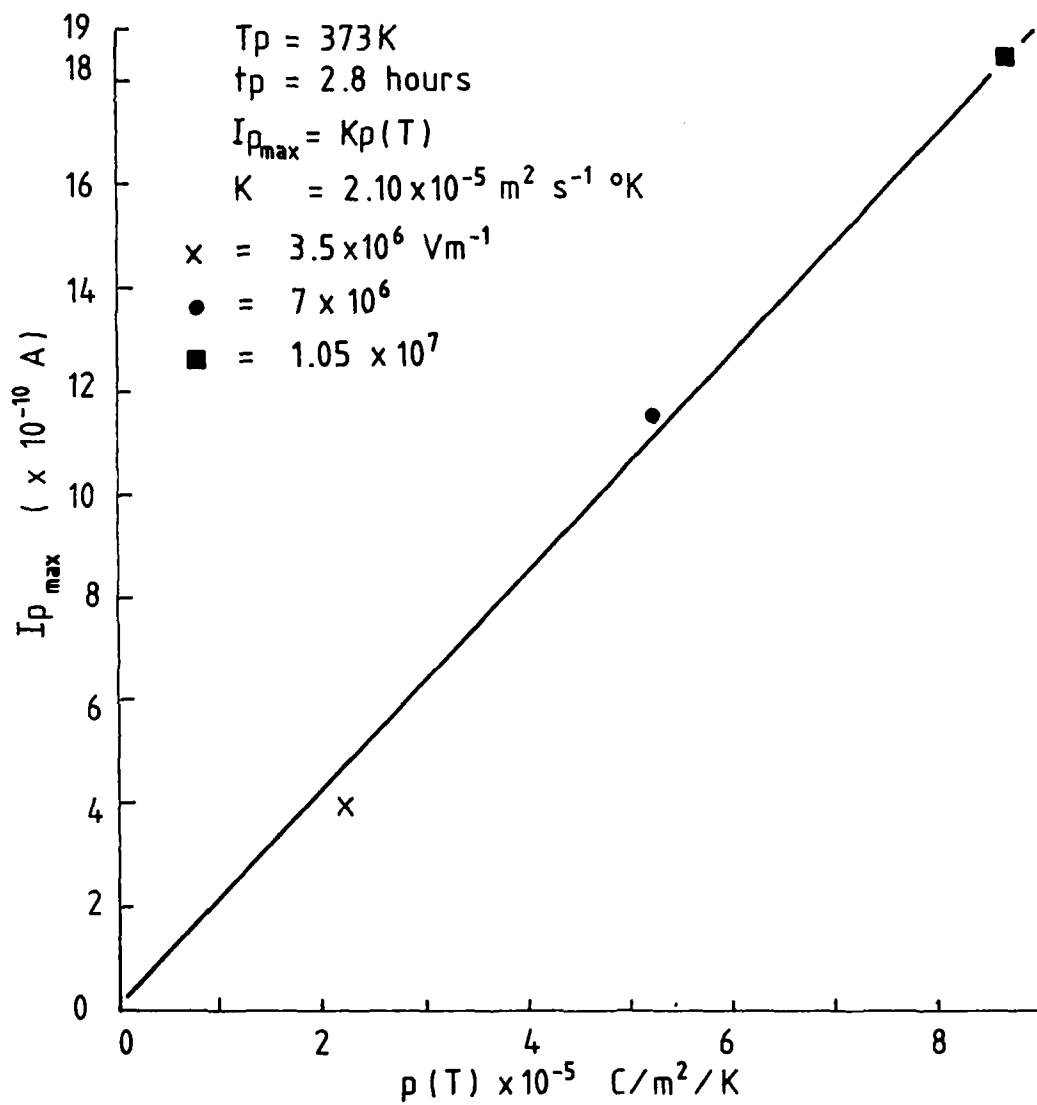


Fig. 5: Peak current against pyroelectric coefficient at 333K in PZT5/PVDF (A) (50/50).

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